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Preliminary Results

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Potentiometric Titration of Gallium  
with Cetylpyridinium Chloride:  
Preliminary Results\*

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Milligram amounts of gallium were titrated potentiometrically in hydrochloric or hydrobromic acid with cetylpyridinium chloride. The indicating electrode was a graphite rod coated with poly(vinylchloride) and dioctylphthalate. Indium is not precipitated under similar conditions and hence does not interfere.

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## INTRODUCTION

Finston and Rahaman (1) have determined gallium by extraction with tetraphenylarsonium chloride ( $\phi_4\text{AsCl}$ ) from hydrochloric acid medium. Complete extraction was accomplished from  $\geq 2.5\text{M}$  hydrochloric acid. We have previously found that many ions that can be precipitated with  $\phi_4\text{AsCl}$  can be titrated potentiometrically with cetylpyridinium chloride (CPC) (4, 6). In fact, the precipitates with CPC are less water-soluble than those with  $\phi_4\text{AsCl}$ ; thus the former yield steeper titration curves. In this work we report the successful potentiometric titration of milligram amounts of gallium in hydrochloric or hydrobromic acid.

## EXPERIMENTAL

The indicating electrode was a spectrographic graphite rod coated with a solution of poly(vinylchloride) and dioctylphthalate in tetrahydrofuran, as previously described (3, 5). The reference electrode was a double-junction Ag/AgCl electrode (Orion No. 90-01) with a 0.1 M sodium nitrate salt bridge. The titration system was controlled by a Tektronix 4051 graphics computer system which has previously been described (2). Titration rates were kept constant at 0.3 ml/min. Stirring was provided by a magnetic stirrer. The stirring motor was isolated from the titration vessel by a water-cooled plate and a grounded aluminum plate. Titration endpoints were calculated as previously described (2). However, any convenient pH/millivolt meter can be used as the measuring instrument.

The titrant was a 0.01 M aqueous solution of CPC. Gallium solutions were atomic absorption standard solutions containing 1.5% (v/v) nitric and 1.4% (v/v) hydrochloric acids. All other chemicals were of the highest purity available. All determinations were made in a volume of 25 ml.

## RESULTS AND DISCUSSION

We have previously presented many applications of CPC in the potentiometric titration of anions, and of cations which can easily be converted to anions, such as cyanides and halides (4, 6). Examples of the former are perchlorate, fluoroborate, and hexafluorophosphate; examples of the latter are platinum hexachloride, aurocyanide, and ferrocyanide. Many anions which were previously determined gravimetrically with  $\phi_4\text{AsCl}$  (8) can, in fact, be titrated with CPC. In this work we show that gallium, which was previously extracted with tetraphenylarsonium chloride from hydrochloric acid medium (1) can also be determined by potentiometric titration with CPC.

Complete extraction of gallium was previously accomplished from  $\geq 2.5$  M hydrochloric acid. In the presence of 2.5 M lithium chloride, complete extraction occurs at  $\geq 0.25$  M hydrochloric acid. We obtained good titration curves with CPC in concentrated hydrochloric acid. Lower acid concentrations yielded progressively poorer curves. As the acid concentration was decreased, increasing amounts of lithium chloride

were required for satisfactory titration curves. We consider 3 N hydrochloric acid in the presence of 5 g of lithium chloride per 25 ml (approx. 4.7 M chloride) the lowest feasible acid concentration for the titration of gallium vs CPC. In 48% hydrobromic acid (approx. 8.2 N) fair titration curves were obtained, which probably can be enhanced by the addition of lithium bromide.

Data for the recovery of 2.00 mg of gallium in various media are presented in Table 1. A representative titration curve for 2 mg of gallium in 6 N hydrochloric acid in the presence of 2 g of lithium chloride is shown in Fig. 1. Indium under the same conditions did not yield a precipitate nor a titration curve. Gallium can, therefore, be determined in the presence of large amounts of indium.

The precipitates formed during the titration could not be isolated because no suitable wash solution could be found (strong acid will destroy the filter paper; water will dissolve the precipitate). They are assumed to be  $C_{21}H_{38}NGaCl_4$  and  $C_{21}H_{38}NGaBr_4$ , based on the stoichiometry of the reaction. It is of interest to note that in potentiometric titrations vs sodium diethyldithiocarbamate (7), while both indium and gallium form stoichiometric precipitates, only indium can be determined potentiometrically. In the titration vs CPC, gallium is present as the halogen anion; in the titration vs diethyldithiocarbamate, it is present as the trivalent cation, and the precipitate formed is  $Ga(C_5H_{10}NS_2)_3$ .

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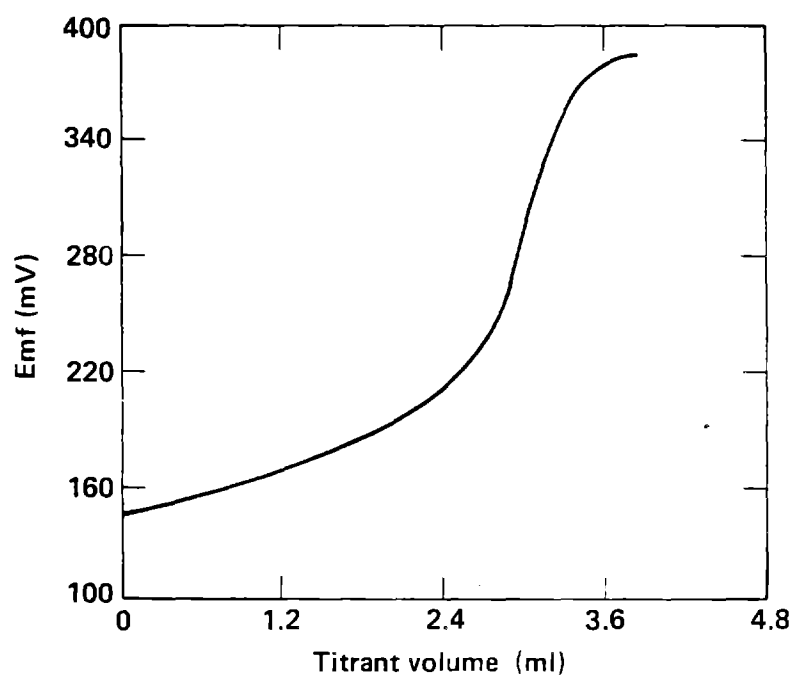


Figure 1. Titration curve of 2.0 mg of gallium in the presence of 2 g of lithium chloride in 6 N hydrochloric acid.

TABLE 1

Statistics for the Recovery of 2 mg of Gallium from Various Media

Medium	Mean recovery, mg	Standard deviation	Number of replicates	Percent. recovery
Concentrated HCl	2.000	0.011	5	100.0
6 N HCl + 2 g LiCl	1.976	0.002	6	98.8
3 N HCl + 6 g LiCl	1.997	0.013	7	98.9
48% HBr	2.113 <sub>5</sub>	0.015	6	105.7